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by

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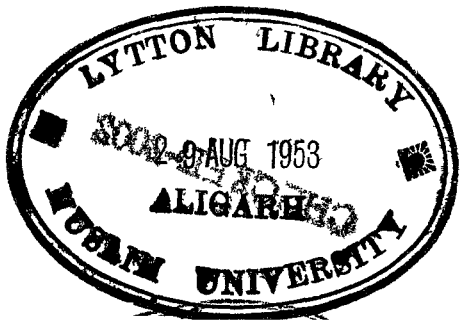


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# T H E O R E T I C A L

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Chemical Composition of Oil:-

All vegetable oils are generally composed of mixtures of saponifiable and unsaponifiable parts.

The saponifiable parts of oil are glyceryl esters of saturated and unsaturated acids. These esters can be hydrolysed into glycerine $C_3H_5(OH)_3$ and fatty acids, generally containing an even number of carbon atoms, such as oleic acid $C_{18}H_{34}O_2$, stearic acid $C_{18}H_{36}O_2$, palmitic acid $C_{16}H_{32}O_2$, linoleic acid $C_{18}H_{32}O_2$, and linolenic acid $C_{18}H_{30}O_2$. These esters are called "glycerides". The glycerides may either be fluid or solid at ordinary temperature. Because the principle parts of oil are the neutral glycerides of the fatty acids, it is expressed by the general formula $C_3H_5(OOCR')$, wherein R' indicates a monovalent hydrocarbon. In addition they may also contain free fatty acids.

In the non-drying oils (olive, almond, peanut etc). glycerides of acids with some unsaturated linkings occur; in the semidrying oils ( cotton seed, sesame, kapok, corn) glycerides of more unsaturated acids together with the glycerides of oleic acid are present; while the drying oils (linseed, hemp seed, poppy seed, sun-flower, tung) contain glycerides of extremely unsaturated acids (linoleic, linolenic) together with olein.

All vegetable and animal fats and oils contain small amounts of unsaponifiable bodies, alcohols and hydrocarbons; characteristic are the sterols which are used in determining the animal or vegetable origin of the fat. The sterols include cholesterol, phytosterol and similar alcohols of high molecular weight. Sterol esters appear to exist in considerable amount only in vegetable oils.

The unsaponifiable material left after separation of the sterols may be 45 to 67 per cent of the total unsaponifiable matter in the case of vegetable oils. Associated with the laevo-rotatory sterins occur dextro-rotatory unknown alcohols and small amounts of hydrocarbons. The composition of vegetable oils and fats derived from one in the same species of plants will fluctuate somewhat with the variety of the plant, the climate and the soil in which it is grown. The physical and chemical properties of the oils are determined by their components.

Methods for the separation of the constituents of the oil:-

(i) Separation of Glycerides:-

(a) The solid glycerides are separated by pressing cold

(b) Some glycerides are separated by the method of distillation at a very low pressure.

(ii) Separation of acids:-

The fatty acids are separated as salts of the alkali metals by a method known as "Saponification" which consists

in boiling the oil with strong bases. The chemical change which oil undergoes on being hydrolysed or saponified is expressed by the following equation:-

$$C_3H_5\begin{matrix}O\cdot R\\O\cdot R\\O\cdot R\end{matrix} + 3\,M\cdot OH = C_3H_5\begin{matrix}O\cdot M\\O\cdot M\\O\cdot M\end{matrix} + 3R\cdot OH.$$

where R denotes the radical of any fatty acid and M stands for hydrogen ( or a monovalent metal).

(iii) Separation of unsaponifiable matter:-

(a) The unsaponifiable matter is separated by extraction from the aqueous alcoholic soap solution with ether. The ether extract can be purified by crystallization from alcohol.

(b) Separation of sterins by Windaus digitonin method (Muller, hydrocarbon, oils and saponifiable fats 2nd edition p. ).

The digitonin is added in alcohol solution to an alcohol solution of the unknown; the sterol precipitates in combination with the digitonin.

More direct is the method of Klostermann and Optiz in which by direct precipitation from the fat is obtained the free or uncombined sterol and by precipitation from the fatty acids after saponification of the fat there is obtained the total content of sterol; free sterol but not a fatty acid ester of it will react with digitonin.

(iv) Separation of hydrocarbons:-

There is no hard and fast rule for the separation of hydrocarbon from the oil. The only method is to extract the unsaponifiable matter from the soap solution of the acids, with ether. The ether extract can be crystallised

from alcohol, if solid or it can be distilled under reduced pressure. Sometimes the boiling points of the hydrocarbons are so close that it becomes very difficult to separate them by distillation. In such cases the methods described below are important.

1. After the separation of acids and the sterols, the unsaponifiable matters are shaken with ninety five per cent alcohol which completely dissolves the benzene hydrocarbons but has very slight solvent action upon the paraffins. The mixture separates into two layers, the one being a solution of the benzene hydrocarbon in alcohol, the other mainly the paraffin. The layers are separated and then separately shaken up with an excess of water. Generally the upper layer consists of the paraffin hydrocarbon and the lower one of the benzene hydrocarbon

2. The most certain method is to treat the mixture with fuming sulphuric acid. The benzene hydrocarbon is converted into a sulphonate, which is soluble in water, the paraffin being unacted upon. To recover the aromatic hydrocarbon, the aqueous solution, after separation of paraffin, is treated with excess of lime, the mixture evaporated to dryness and the calcium salt subjected to dry distillation, when the hydrocarbon distils over. Or in some cases the sodium salt of the sulphuric acid can be obtained by pouring the strong acid solution into a

saturated solution of sodium chloride. The sodium salt of the sulphonate of the aromatic hydrocarbon separates out and may be filtered off. The paraffin hydrocarbon floats upon the surface of the aqueous solution and may be separated in any appropriate manner.

3. Another way is to treat the mixture of hydrocarbons with a mixture of equal volumes of concentrated nitric and sulphuric acids. If the reaction becomes too vigorous, the mixture should be cooled. Finally when the reaction ceases, it should be heated on the water bath for a few minutes. Then the mixture will be poured into cold water and the oily layer will be separated from the aqueous layer. The nitro compound is now reduced with tin and hydrochloric acid until its smell vanishes. The amido compound so produced remains dissolved in the acid solution. The paraffin can be extracted by means of ether. The amido-compound can now be obtained by rendering the acid solution alkaline and extracting with ether

4. Sometimes after having the soap, the whole substance should be poured into an excess of saturated salt solution and steam distilled. The sodium salt of the fatty acids remains behind and the unsaponifiable oils distil over with steam and may then be separated as above described.

Methods for de-odorising oils :-

1. At present the malodorous gases present in suspension in fats and oils can be removed by a specially made apparatus

known as "Filbert's Deodorising apparatus" (Louis E. Andes, Vegetable fats and Oils, p. 285).

2. Stephenson's Method of De-odorisation:-

For purifying and deodorising the oil, a composition is prepared by granulating together alumina ( free from lime), magnesia and iron, incorporating this mixture with imperfectly burnt charcoal containing organic matter, and the whole heated in closed retorts, which are then allowed to cool down before being opened.

3. De-odorising with gases:-

It is well known that oils and fats and other similar bodies can be deprived of smell by the action of steam. Nevertheless, it has not, so far, been possible to prepare by this means oils and fats of unimpeachable quality for alimental purposes, since, although the smell of the substance is removed, the subsequent development of a rancid flavour cannot be prevented. However, since the opinion has been formed that rancidity is caused by the action of atmospheric oxygen mixed with the steam, the possibility of combating this evil by treating the oil with superheated steam in the absence of air has become apparent. The oil is heated in suitable vessels, in which a vacuum may be produced, or through an inert gas ( nitrogen, carbon monoxide, carbonic acid, hydrogen, etc) is passed and as soon as

the air is removed, the temperaturation is raised to between 110 and 220 c according to circumstances and a current of superheated steam passed through the liquid mass until the condensed water is perfectly inodorous. As soon as this is accomplished the steam is shut off and the oil cooled in presence of an atmosphere of the gas employed before.

4. De-odorising by Agitation:-

The method of agitating rancid or evil-smelling oils with amyl alcohol ( 90,88 and 86 per cent strength) gives very good results. As a rule an 85 to 87 per cent pure spirit is sufficient, since it dissolves most of the fatty acids.(Andes, Vegetable Fats and Oils; p.238).

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The present work on Neem oil was undertaken with a view

1. To investigate the nature of the products obtained on decomposition of Neem oil,
2. To examine the unsaponifiable constituents of neem oil,
3. To study the odoriferous substance in neem oil and
4. To find some representative method of preparing soaps.

Genuine samples of Neem oil in quantity used in this investigation were procured from the local market.

So far the work done on Neem oil, was the separation of fatty acids and bitter principle of the oil. It appears that none has attempted up to this time to investigate the composition of unsaponifiable matter in Neem oil. So the present work of the author, though difficult, was very important.

On distillation on direct flame, the neem oil gave both solid and liquid glycerides, ester of acids, liquid and gaseous hydrocarbon of both saturated and unsaturated linkings and some gaseous aldehyde.

Gaseous hydrocarbon and aldehyde escaped within the temperature of 110°-140° c and above this temperature no gas evolved. The substance which distilled at 100°-110° c was possibly a sulphur compund. At the temperature when gaseous products escaped, only liquid substances, possibly hydrocarbons, and glycerides or ester of acids distilled. Again some hydrocarbons accompanied by solid glycerides distilled at 140°-205° c.

On fractional distillation, a hydrocarbon of ethylene series having the general formula $C_nH_{2n}$ was obtained. The molecular weight of this hydrocarbon was 195 and its molecular formula appeared to be $C_{14}H_{28}$. It was a saturated liquid hydrocarbon having b.p. 100-110 c/47 mm. of Mercury. It was insoluble in sulphuric acid and was much more aliphatic than the aromatic hydrocarbons. The hydrocarbon formed the bromo-derivative which did not melt but decomposed at high temperature. Oxidation of this product gave some acids and aldehyde.

The portions distilling over 200° c were possibly hydrocarbons of high molecular weight. From the physical and chemical properties of two substances it appeared that they were hydrocarbons. One substance, b.p. 150-155° c / 3.3 mm. of Mercury has molecular weight 239.55 and the other b.p. 142-152° c has molecular weight 339.5.

The percentage of the gaseous products, the distillate and the residue, obtained on distillation, is given below:-

1. Distillate consisting of both solid and liquid products = 77-78 %
2. Black tarlike residue = 7-8.7 %
3. Gaseous product = 13-15.3 %

On distillation, a fatty acid ester of an alcohol which has the molecular weight 169.6 was obtained. When the distillate obtained from Neem oil was subjected to a process of steam distillation directly, no alcoholic substance was found, in the steam distillate. But when the distillate, after the treatment with caustic soda, was steam distilled, the alcoholic substance was obtained in the products, distilled over with steam. This experiment showed that the alcohol b.p. 120-125° / 13.5 mm. of Mercury was in ester form.

# S U M M A R Y

A small quantity of oleo margosa from Melia Azadirachta or neem oil was distilled at ordinary pressure on direct flame and the distillate was again fractionated under reduced pressure. The physical constants of some particular fractions, found out were given in the table below. The chemical behaviours of these substances towards some reagents, were studied. Of these substances, a hydrocarbon of molecular formula $C_{14}H_{28}$, belonging to ethylene series was identified.

Another quantity of neem oil was distilled and the distillate was saponified with alcoholic caustic soda solution. The unsaponifiable matter was extracted with ether from the soap. The ether was recovered and the residual oil was subjected to a process of steam distillation. The product obtained on steam distillation was dehydrated over anhydrous sodium sulphate and then fractionated under reduced pressure.

The chemical behaviours of these fractions were studied. From the chemical behaviours, a substance of molecular weight 169.6, appeared to be alcohol. The physical constants of this product were found out and given in the table below:-

T A B L E.

| Sample No. | Density at different temperature. | Refractive Index | Freezing point. in c | Boiling point in ° c | Surface Tension dynes per cm. | Molecular weight. |
|---|---|---|---|---|---|---|
| 6 | (0.8383/18° c<br>(0.8276/ 45° c<br>(0.8324/ 30° c | 1.3110 | -7° - -8° c | 142-152 | (25.08@ 30° c<br>(24.36@ 45 c | 339.5 |
| 7 | (0.8042/15° c<br>(0.7840/40° c | 1.3122 | -9° | 100-110 | (35.8 @ 15 c<br>(28.08@ 40 c | 195 |
| 8 | (0.8422/ 19°c<br>(0.8389/45° c | 1.3134 | -3° | 110-120 | | |
| 10 | (0.8512/30° c<br>(0.8415/45° c | 1.3120 | 2° | 150-155 | (20.75@ 30 c<br>(19.8 @ 45 c | 239.55 |
| Substance containing alcoholic group. | (0.7885/15° c<br>(0.78202/40° c | 1.3125. | x | 120-125/13.5 of Mercury | (23.67@15 c<br>(22.70@40 c | 169.6 |

For the removal of the obnoxious odour of neem oil, several methods were tried in which the method of washing the oil with dilute sulphuric acid and then with sodium bisulphite followed by alcohol and water was successful to a great extent.

From crude neem oil, soap was prepared which appeared indeed to be good in quality.

# E X P E R I M E N T A L

## Preparation of Soap.

The crude neem oil was treated with ordinary alcohol and the alcoholic layer was separated. The residual oil was then subjected to saponification with caustic soda in a vessel heated in a water bath for a long time.

When the saponification was complete, excess of sodium chloride was added and soap floated on the surface of the mixture. The soap was separated and washed with brine several times and then with water until the excess of alkali was removed.

The soap was then taken out and pasted well and dried and finally given some form.

The soap prepared in this way from neem oil contains imperceptible odour of the original oil.

## Nature of the gas resulting from the decomposition of neem oil.

(a) A considerable quantity of neem oil was heated on the direct flame; the gas evolved from the decomposition of the oil was collected and examined as follows:-

1. The gas possesses very nauseating and penetrating smell and causes immediate headache if inhaled in large quantities.

2. The gas gives pink colour with Schiff's reagent and decolourises the potassium permanganate solution.

3. It is not absorbed in water but absorbed to some extent in ordinary alcohol which shows all the above mentioned reactions. On standing for some days, the alcoholic solution loses the reactivity.

4. It is inflamable and ligher than air.

(b) In order to estimate the percentage of the gaseous products, the following two experiments were made:

(i) Weight of the distilling flask alone = 141.7 gm.

Weight of the distilling flask and the residue after distillation = 157 gm.

Weight of the residue = 15.3 gm.

Weight of the receiver alone = 133.9 gm.

Weight of the receiver and the distillate = 175 gm.

Weight of the distillate = 41.1 gm.

Weight of the second receiver alone = 147.7 gm.

Weight of the receiver and the distillate = 242.5 gm.

Weight of the distillate = 94.8 gm.

Weight of the third receiver alone = 63.8 gm.

Weight of the receiver and distillate = 81.9 gm

Weight of the distillate = 18.1 gm.

Total weight of the distillates and the residue = 169.3 gm

Out of two hundred gms. of oil, 169.3 gm. of the products were obtained and the rest was the gas and hence the percentage of gas was 15.35.

(ii) Two hundred gms. of oil was taken and the same experiment was made:

| | |
|---|---|
| Weight of the receiver alone | = 147.7 gm |
| Weight of the receiver and the distillate | = 264.6 gm |
| Weight of the distillate | = 116.9 gm |
| Weight of the receiver alone | = 133.9 gm |
| Weight of the receiver and the distillate | = 156.5 gm |
| Weight of the distillate | = 22.6 gm. |
| Weight of the receiver alone | = 54.5 gm. |
| Weight of the receiver and the distillate | = 71.4 gm |
| Weight of the distillate | = 16.9 gm. |
| Weight of the distilling flask alone | = 141.5 gm. |
| Weight of the distilling flask and the residue | = 159 gm. |
| Weight of the residue | = 17.5 gm. |
| Total weight of the distillate and the residue | = 173.9 gm. |
| Weight of the gas evolved from two hundred gms. of oil | = 26.1 |
| Percentage of gas | = 13.05 |

The percentage of gas found from these two experiments was 13-15.

## Fractionation of Neem oil.

Two hundred gms. of crude neem oil were distilled at ordinary pressure on the direct flame and the distillate was collected at five degree range of temperature. These fractions were again fractionated at reduced pressure by

using a glycerine bath. The fractions collected at different temperatures and pressures are shown below:-

| Test tube No. | Temperature in ° c. | Pressure in mm. of Hg. |
|---|---|---|
| 1. | 55-60 | 8.77 |
| 2. | 75-80 | 8.77 |
| 3. | 90-95 | 9.27 |
| 4. | 95-110 | 17.27 |
| 5. | 110-120 | 16.27 |
| 6. | 130-135 | 17.27 |
| 7. | 100-110 | 4.7 |
| 8. | 110-120 | 6.7 |
| 9. | 130-135 | 4.2 |
| 10. | 150-155 | 3.3 |
| 11. | 157-161 | 4.25 |
| 12. | 199-201 | 6.25 |
| 13. | 205-210 | 6.25 |

The distillates No. 12 and 13 solidified at room temperature

M.P. of fraction No. 12 — 31 c (sharp)

M.P. of fraction No. 13 — 38 c (sharp)

In all the above cases a little amount of residue was left over in the distilling flask.

The first two fractions collected at temperatures (55-60) and (75-80) have very peculiar penetrating smell which produces immediate headache on inhalation.

They are acidic in character and decolourise potassium permanganate solution as well as a solution of bromine in chloroform. They reduce Fehling's solution and do not give any precipitate with the sodium bisulphite solution..

They are possessed of great insecticittal reactivity.

Determination of the refractive index of fractions Nos.6,7,8 and 10 at room temperature by Jamans Refractometer.

| | | |
|---|---|---|
| | Room temperature | = 15.7 c |
| 1. | Refractive Index of fraction No.6 | = 1.3110 |
| 2. | Refractive Index of fraction No.7 | = 1.3122 |
| 3. | Refractive Index of fraction No.10 | = 1.3120 |
| 4. | Refractive Index of fraction No.8 | = 1.3134 |

Determination of the density of fractions Nos.6, 7,8 and 10 at different temperatures.

The apparatus used for this purpose is diagrammatically shown below:

I. Sample No.6.

(a) Weight of the pyknometer alone = 6.0934 gm.

Weight of the pyknometer + water upto to the mark at 18 c = 6.9069 gm

Weight of water at this temperature = .8135 gm.

Weight of the pyknometer + oil at 18 c = 6.7754 gm.

Weight of the same volume of oil at same temperature = .6820 gm.

Density of this fraction at 18 c

= .6820/.8135 = .8383

(b) Weight of the pyknometer + water at 45 = 6.9027 gm.

Weight of water at this temperature = .8093 gm.

Weight of the pyknometer + oil at 45 c = 6.7632 gm.

Weight of oil at this temperature = .6698 gm.

Density of this fraction at 45 c

= .6698/.8093 = .8276

(c) Similarly the density of this fraction of oil at 30 c was found to be 0.8324.

II. Sample No.7.

(a) Weight of the pyknometer alone = 6.0736 gm

Weight of the pyknometer + water at 15 = 6.9062 gm.

Weight of water at 15 c = .8326 gm.

Weight of pyknometer + oil at 15 c = 6.7432 gm.

Weight of oil at this temperature = .6696 gm.

Density of this fraction at 15 c

= .6696/.8326 = 0.8042

(b) Weight of the pyknometer + oil at 40 c = 6.7224 gm

Weight of oil at this temperature = .6488 gm.

Weight of the pyknometer + water at 40 c = 6.9012 gm

Weight of water at this temperature = .8276 gm

Density of this fraction of oil at 40 c

= .6488/.8276 = 0.7840

III. Sample No.8.

(a) Weight of the pyknometer alone = 6.0794 gm

Weight of the pyknometer and water at 19 c. = 6.8929 gm

Weight of water at 19 c = 0.8135 gm

Weight of the pyknometer + oil at 19 c = 6.7646 gm

Weight of oil at this temperature = .6852 gm

Density of this fraction of oil at 19 c

= .6852/.8135 = 0.8422

(b) Weight of the pyknometer + oil at 45 c = 6.7584 gm

Weight of oil at 45 c = .6790 gm

Weight of pyknometer + water at 45 c = 6.9027 gm

Weight of the water at 45 c = .8093 gm

Density of this fraction of oil at 45 c

= .6790/.8093 = .8389

IV. Sample No.10.

Similarly the densities of this fraction of oil were found out at 30 and 45 c which were respectively equal to 0.8512 and 0.8415 .

## Determination of the Surface Tension of fractions Nos. 6,7 and 10.

### Sample No.7.

The surface tension of this fraction of oil was calculated at two different temperatures from the following relation:-

(Surface Tension) = ½ x h x r x d x g dynes per cm.

Where h = height of the column of oil, rises in the capillary tube and was found from the reading of the Cathetometer

r = radius of the capillary tube and found out by the help of the travelling microscope

d = the density of the oil

g = Gravitation constant.

| Sample No. | Height through which the column of oil rises | Density | Temperature | Radi |
|---|---|---|---|---|
| 6. | 2.273 cm | .8324 | 30 c | .02765 |
| | 2.17 cm | .8276 | 45 c | .02765 |
| 7. | 4.32 cm | .8042 | 15 c | .021 |
| | 3.47 cm | .7840 | 35 c | .021 |
| 10. | 2.693 cm | .8512 | 30 c | .0184 |
| | 2.60 cm | .8415 | 45 c | .0184 |

(a) The surface tension of the fraction No.7 at 15 c and 40 c as was calculated from the above mentioned formula were respectively equal to 35.8 and 28.02 dynes per cm.

Sample No.6.

By the same method as above, the surface tension of this fraction was found

Surface tension at 30 c = 25.08 dynes /cm

Surface tension at 45 c = 24.36 dynes /cm

Sample No.10.

Surface tension of this fraction, found out in the same manner at 30 c = 20.75 dynes /cm

Surface tension at 45 c = 19.8 dynes / cm

Determination of the molecular weight of fractions Nos.7,6 and 10.

Sample No.7.

Then knowing the surface tensions and the densities of this fraction of oil at two different temperatures, the molecular weight of the substance was calculated from the following formula:-

$$\frac{\gamma_1(Mv_1)^{\frac{2}{3}} - \gamma_2(Mv_2)^{\frac{2}{3}}}{t_2 - t_1} = 2.12$$

Where M = molecular weight of the substance

$V_1$ & $V_2$ = the specific volumes of the substance at two temperatures.

The molecular weight of this fraction as calculated from the above formula = 195.

Sample No.6.

By using the same formula; the molecular weight of the fraction No.6 was calculated and found to be equal to 239.5

Sample No.10.

Similarly the molecular weight of the sample No.10 as calculated from the above formula = 239.5

## Identification of the fraction.

Sample No.7.

1. This substance has a peculiar smell resembling kerosine oil. It is almost colourless when freshly distilled but on standing it develops slightly violet colour.

2. It decolourises potassium permanganate solution as well as the solution of bromine but it does not impart any colouration to Schiff's reagent.

3. The substance does not reduce Fehling's solution nor the ammonical solution of silver nitrate. It does not react with the solution of sodium bisulphite and so it has got no aldehydic group.

4. The substance is neutral and does not react with sodium bicarbonate nor it gives any reaction with calcium chloride and ferric chloride solution. Hence it does not contain any carboxylic group.

5. Metallic sodium has got no action on the pure and dry sample of this substance and so no alcoholic group is present in this substance.

6. The substance has no oxygen in the molecule which may be inferred from the result of the combustion of the substance.

7. Since the original oil contains no nitrogen and halogen except sulphur which is also absent from this fraction, it may be concluded here that the product is a hydrocarbon.

8. When 5 p.c. solution of bromine in chloroform was added to a small quantity of the substance in chloroform, a white precipitate was formed. The precipitate was immediately filtered and dried. This bromo-derivative does not melt but decomposes at high temperature. The precipitate in solution, on keeping for some hours, becomes black and gives an odour which produces coughing. The precipitate on both conditions was preserved.

9. With ammonical copper sulphate solution it gives immediate blue precipitate.

10. Two or three drops of concentrated hydrochloric acid in alcohol when added to a small quantity of this substance in alcohol, a pink colour appeared with slight turbidity.

11. To a small portion of the substance, a few drops of glacial acetic acid and amyl nitrite were added and then further 5 c.c. of glacial acetic acid followed by fuming hydrochloric acid. No precipitate appeared i.e. it does not give any nitroso-chloride derivative which is the characteristic test for the hydrocarbon of the terpine group.

12. On adding excess of bromine solution to the substance, hydro-bromic acid is evolved showing that the substance is saturated.

## Determination of the empirical formula of the substance by combustion method:

Sample No.7.

To determine to empirical formula of the substance the following two experiments were made:-

| | | |
|---|---|---|
| I. (a) | Weight of the calcium chloride tube before absorption of water | = 60.4836 gm. |
| | Weight of the calcium chloride tube after the absorption of water | = 60.6120 gm |
| | Weight of water formed | = 0.1284 gm. |
| (b) | Weight of carbosorb tube before absorption of carbon dioxide | = 69.0936 gm |
| | Weight of carbosorb tube after absorption of carbon dioxide | = 69.3430 gm |
| | Weight of carbon dioxide absorbed | = 0.2494 gm. |
| (c) | Weight of the glass bulb, empty | = 1.7624 gm |
| | Weight of the bulb and substance | = 1.8372 gm. |
| | Weight of the substance taken | = .0748 gm. |

Calculation:-

.0748 gm. of the substance gave .2494 gm. of carbon dioxide and .1284 gm. of water.

The percentage of carbon in the substance

$$= \frac{12 \times .2494 \times 100}{44 \times .0748} = \frac{12 \times 2494 \times 100}{44 \times 748} = 90.90$$

The percentage of hydrogen in the substance

$$= \frac{2 \times .1284 \times 100}{18 \times .0748} = \frac{2 \times 1284 \times 100}{18 \times 748} = 19.07$$

II. (a) Weight of the glass bulb, empty = 1.9344 gm

Weight of the glass bulb and substance = 2.0554 gm

Weight of the substance taken = 0.1210 gm

(b) Weight of the calcium chloride tube before absorption of water = 60.6120 gm

Weight of the calcium chloride tube after the absorption of water = 60.7884 gm

Weight of water absorbed = 0.1764 gm

(c) Weight of the carbosorb tube before the experiment = 68.9371 gm

Weight of the carbosorb tube after the experiment = 69.3199 gm

Weight of carbon dioxide absorbed = 0.3828 gm

Calculation:-

0.1210 gm. of the substance gave 0.3828 gm of carbon dioxide and 0.1764 gm. of water.

The percentage of carbon in the substance

$$= \frac{12 \times .3828 \times 100}{44 \times .1210} = \frac{12 \times 3828 \times 100}{44 \times 1210} = 86.3$$

The percentage of hydrogen in the substance

$$= \frac{2 \times 0.1764 \times 100}{18 \times .1210} = \frac{2 \times 1764 \times 100}{18 \times 1210} = 16.2$$

From these two experiments, the empirical formula of the substance will be $CH_2$

Molecular weight by this formula = 14

The molecular formula of this substance will be $(CH_2)_{14}$ = $C_{14}H_{28}$.

Oxidation of the hydrocarbon and the study of the products.

( 1) A little of the substance was taken in a test tube and oxidised with potassium permanganate solution. To this mixture water was added and the whole substance was shaken well. Now the oily layer was separated from the rest of the solution which gave the following tests.

1. To a small quantity of Fehling's solution, the oxidation product was added and the mixture was heated when the Fehling's solution was reduced showing that it contained some aldehydic substance.

2. The solution of the oxidation product was acidic and made neutral with caustic soda solution. To a little of this neutral solution, when calcium chloride solution was added, a white precipitate, very small in quantity was formed. On adding acetic acid, the precipitate dissolved away. This test indicates the presence of tartaric acid in the oxidation product.

3. The solution of oxidation product did not give any reaction with ferric chloride solution.

4. To ammonical solution of silver nitrate the solution was added and the mixture was kept in the hot-water bath. No mirror was formed but some precipitate came out.

(II). Separation of unsaponifiable oil and its fractionation.

The crude neem oil was distilled at ordinary pressure on the direct flame and the distillate was collected in the same receiver.

Since some distillate solidified at room temperature, they were filtered at the pump and pressed. On keeping the filtrate, there appeared some solid again which was again separated by filtration.

After the separation of the solid portion, the oil was treated with alcoholic caustic soda in a round bottom flask and heated for about two hours with a reflux condenser, on a water bath. When the saponification was complete, the mixture was cooled and transferred to a distilling flask and the alcohol was completely distilled off from the mixture.

The residual substance was then treated with ether and the ethereal layer was separated by means of a separating funnel. This process was repeated several times to ensure the complete separation of unsaponifiable oil from the sodium salt of unknown acids. The sodium salt was kept as such.

From the ethereal solution, the ether was completely recovered and the remaining unsaponifiable oil which did not distil at ordinary pressure, was subjected to steam-distillation. The oil distilled over with steam.

The oil which came out for the first few hours with the steam was greenish yellow and possessed good smell. When it was found that the good smelling portion ceased to distil, the receiver was changed and the distillate of yellow colour was collected in separate receiver. In the above distillation, some amount was left over in the flask undistilling with steam.

I. The first portion of the steam distillate was dehydrated over anhydrous sodium sulphate and distilled under reduced pressure. The distillate was collected at different constant temperatures.

Fraction No.I:- Collected between 97-100° c at pressure 16.2 mm. of Mercury.

Properties of this fraction:-

1. The product is colourless and possesses sweet smell. It decolourises potassium permanganate solution as well as the solution of bromine in chloroform.

2. The substance contains no alcoholic group nor the aldehydic group.

3. It has no carboxylic group and it is neutral.

Fraction No.II. Collected between 120-125 c at pressure 15.2 mm. of Mercury.

1. This fraction has got slight blue colour which does not change on standing. The substance has sweet smell and is neutral.

2. It has no carloxylic and aldehydic group.

3. It is free from sulphur.

4. The substance does not react with bromine nor with hydrochloric acid.

5. When a piece of metallic sodium was dropped in a dry and pure sample of this substance it gave effervescence showing that it contained alcoholic group.

6. In presence of pyridine, benzoyl chloride ($C_6H_5COCl$) was added to a little of the substance and the mixture was heated on a water bath for about thirty minutes with an air condenser fitted at the mouth of the text tube. Some precipitate was formed which was filtered and crystallised from petroleum ether.

M.P. of the benzoyl derivative 40 c (sharp).

The following constants were found:-

1. Refractive Index at 15.7 = 1.3125

2. Density = (0.78885/15 c
(0.78202/40 c

3. Surface Tension = (23.67 dynes/cm. / 15 c
(22.70 " " / 40 c

4. Molecular weight = 169.6

5. The substance does not freeze even at - 15 c.

The product being too small, its further examination was not possible.

To have an idea whether the alcoholic substance was present in the original distillate in this form or in the form of an ester, a considerable quantity of neem oil was distilled and the distillate was subjected to steam distillation without being treated with caustic soda. This time the steam distillate was yellow coloured and possessed bad smell. The distillate was dehydrated over anhydrous sodium sulphate and then fractionated under reduced pressure. All the fractions were tested but no fraction containing alcoholic group was obtained So it is evident that the alcoholic substance was not present as such in the original distillate from neem oil but in some ester form which in the previous experiment; during the treatment of the substance with caustic soda, was converted into alcohol.

II. The second portion of the steam distillate which contains bad odour and is acidic was kept as such.

Removal of the bad odour of Neem oil.

1. After the distillation of the neem oil, it still contains very bad and penetrating odour. For the removal of this bad odour, the distillate was treated with

concentrated sulphuric acid when fruity smell was the characteristic of the substance. After this treatment, the oil was washed well with water several times and then dehydrated over calcium chloride. This oil, free from bad odour did not distil at ordinary pressure and seemed to decompose at high temperature.

2. To remove the bad odour of neem oil, the crude oil was treated with dilute sulphuric acid several times and then washed well with hot water until it became free from acid. After this treatment the oil, still contained bad odour, was treated with sodium bisulphite solution and washed well and then the oil was shaken well with ordinary alcohol and separated from the alcoholic layer and finally washed with water.

The oil, washed in the above mentioned way, became almost free from bad odour.

3. The bad odour may be removed to a large extent by washing the oil several times with glacial acetic acid and then with sodium bisulphite and finally with water.

4. Steam distillation is also effective to remove the bad odour to some extent but not fully.

5. By washing with $HNO_3$, the odour cannot be removed.